INVESTIGATION OF THE PIGMENTS USED IN TWO 16th CENTURY ICONS ATTRIBUTTED TO ONUFRI: NON-DESTRUCTIVE ANALYSIS BY A PORTABLE XRF SPECTROMETER

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Abstract

The studied icons are attributed to Onufri from Neokastra, who is considered the best painter that had ever worked in Albanian territory and one of the best for the whole Balkan region. Onufri is the creator of the "Berati School", a school that expanded not only in central and southern Albania, but also in northern Greece, western Macedonia, etc., becoming one of the most important iconographic schools of the peninsula during the 16-17th centuries. The studied icons are painted with the technique of tempera on wooden support and are exposed at "Onufri" museum in the city of Berati (central Albania). The main objective of the study was the collection of data on the materials used by Onufri that on one hand can help to understand the painting technique and on the other hand can be used for conservation purposes. A portable XRF spectrometer assembled at our laboratory was used for the in-situ non-destructive examination of the icons. The spectrometer is based on a low power X-ray tube, a thermoelectrically cooled Si PIN detector and the spectrum acquisition system. The results of the measurements indicate that the preparation layer was made of gypsum while the palette includes the following inorganic pigments: lead white, gold, yellow and red ochre, vermilion, red lead, a copper based green and probably carbon black.

Key words: XRF spectrometer, inorganic pigments, Icons, Onufri, Berat, Albania.

Introduction

The present work focuses on the investigation of two sixteenth century icons attributed to the famous painter Onufri, exposed at the Onufri museum in Berat. Onufri from Neokastra, is considered the best painter that had ever worked in Albanian territory and one of the best for the whole Balkan region. Onufri is the creator of the "Berati School", a school that became one of the most important iconographic schools of the peninsula during the 16-17th centuries and expanded not only in central and southern Albania, but also in northern Greece, western Macedonia, etc. It is thought that Onufri begun his activity as an icon painter in the city of Berati and later his activity was extended to the decoration of the whole church i. e. wall paintings and icons (Puzanova, 1953 & Popa, 1998). From the works of Onufri have remained wall paintings inscribed by him at "St. Apostles" and "St. Anargyres" churches in Kastoria, Greece (1547), "St. Nicolas" church in Shelcan, and "St. Paraskevi" church in Valsh, both in the district of Elbasan,

Albania (1554). The wall paintings at "St. Theodore" church in Berat, Albania, those of the churches of "Transfiguration" and "St. Nicolas" in Zrze, Prilep, North Macedonia, etc. together with a number of icons, most of which are exposed in the museums of Korca and Berat, are attributed to him due to the very strong similarities with the wall paintings from the churches in Shelcan and Valsh (Puzanova, 1953 & Popa, 1998).

The main purpose of this research was the identification of the materials used by Onufri in these two icons. The identification of the various materials used in paintings is of paramount importance in order to understand the utilized raw material, the painting techniques, and to help their conservation and restoration. While, there have been a number of studies on the materials used in various post-Byzantine icons in Albania (Civici, 2005 & Franceschi *et al.*, 2013) and even on the materials used by Onufri in his wall paintings (Pavlidou *et al.*, 2006 & Civici *et al*., 2008), the information regarding the pigments utilized by Onufri in icons is scarce (Franceschi et al., 2012).

The variety of materials used in Byzantine and post-Byzantine icons have been the subject of a significant number of studies using both destructive and nondestructive analytical techniques (Sotiropoulou, 2010 & Lazidou, 2008). Nowadays, nondestructive examinations that can be performed in-situ are preferred due to restrictions in sample collection from these precious objects. In this study a portable XRF spectrometer is used for in-situ analysis of the decorated areas of the icons. The application of XRF techniques to pigment identification is based on the identification from the spectrum of one or more "key elements", which are the main constituents of the pigment. In most of the cases the combination of color and "key elements" lead to effective inorganic pigment identification. A limitation of the technique is the inability to identify organic pigments due to the insufficient sensitivity of XRF for low Z elements, (Moens *et al.*, 2000 & Klockenkamper *et al*., 1993).

The studied icons

The studied icons are exposed at the Onufri museum in Berat and are painted with the technique of tempera on wooden supports.

The first icon "Christ Pantocrator" (dimensions 134 x 73 cm) is actually the first icon of the iconostasis of the church dedicated to "The Dormition of St Mary" in Berat, where the museum is situated. Christ is depicted in a monumental style as the God-Ruler of the Universe, blessing with the right hand and holding the Bible on the left hand. The background above the figure of Christ is decorated with a silver foil.

The second icon "The presentation of Jesus Christ in the temple" (dimensions 54 x 34.5 cm) is one of the most famous icons of Onufri and belonged to the second registry of icons of the iconostasis of the church of Annunciation in Berat (Mondadori Electa, 2002). In the icon the Virgin accompanied by St. Joseph is presenting Jesus baby in the temple to the priest St. Simeon, who is holding the Child respectfully in his hand

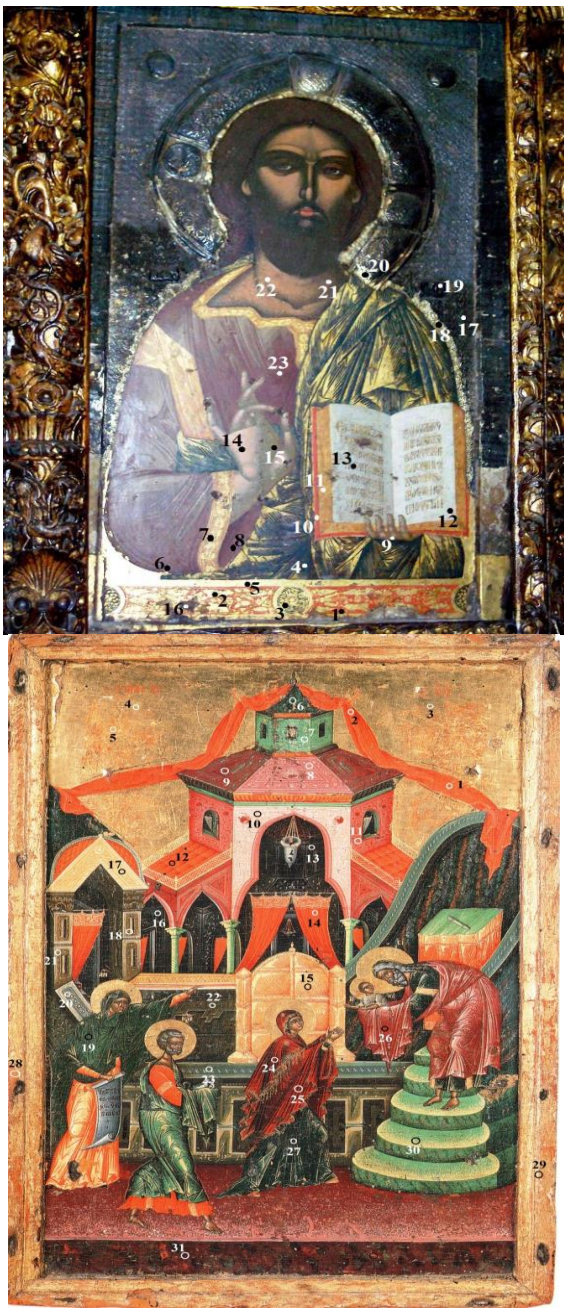

Figure 1. Photos of the icons with the respective positions of the measurements; left icon of "Christ Pantocrator"(KP), right "The presentation of Jesu Christ in the temple" (PKT).

Experimental

The portable EDXRF spectrometer was assembled at our laboratory. It consists of a small thermoelectrically-cooled Si-PIN X-ray detector (model XR-100CR from AMPTEC INC., USA), a self-contained miniature X-ray tube system (ECLIPSE-III) and the signal processing unit.

The Si-PIN photodiode has an area of 7 mm^2, thickness of 300 μm and is thermo- electrically cooled down to -30°C. The hermetic package of the detector has a light tight, vacuum tight 25 μm thick Beryllium window which enables the detection of soft X-rays. The detector energy resolution tests, using a Fe-55 source, showed values of FWHM from 190 to 195 eV for Mn K_α, when the peak count rate is in the range 200–3000 cps and peak to background ratio around 600. The X-ray tube ECLIPSE-III has a silver (Ag) transmission anode, a beryllium end window and has been designed to operate at maximum power of 3 W (30 kV/100 μA).

The signal processing unit consists of a special unit (model PX2CR, AMPTEK), which provides the power supply for the detector and includes a specially designed spectroscopy grade shaping amplifier and a small multichannel analyzer (model Pocket MCA 8000A, AMPTEK) together with the software ADMCA installed in a laptop.

The X-ray tube and the detector were mounted on the geometrical setup in perpendicular directions so that both their axes are intersected on the sample surface at 90^0. The X-ray beam from the tube is collimated through a 4 mm aluminum collimator that allow the positioning of filters and a similar collimator with 2.5 mm hole is used in front of the detector. In this arrangement the spot of the radiation on the sample surface is an ellipsis with diameters of 10 and 6 mm (Civici, 2006). Two laser pointers mounted on both sides of the detector provide for the optimal and repeatable positioning of the sample (laser spots are overlapped on the optimal position). During the measurements the X-ray tube was operated at 30 kV and the current was 10 μA. The primary X-ray radiation was filtered through two foils of Ag and Al of about 0.2 mm thickness. In this way we had a low and flat background in the region 2 - 12 keV, but the low Z elements are not sufficiently excited.

The spectra with sufficient intensity of the main elements were collected for 200 s at each point. During in-situ operations the measuring head of the spectrometer was mounted on a tripod that allowed its correct positioning towards the object. The intensities of the elements showing up in the measured X-ray spectra were calculated by the program AXIL (Van Espen *et al.*, 1977). The intensity of each element was later normalized to the sum of the intensities of all the elements identified in the spectrum. This allows us to have a better idea of the relative intensities of the different elements appearing in the spectrum, making clear the

identification of major elements. On the other side the normalization enables the comparison of the spectra measured at different positions of the icon because it reduces the errors due to not perfect positioning of the measuring head.

Results

In the icon "Christ Pantokrator" we performed measurements at 24 different points, while 31 measurements were performed at the icon "The presentation of Christ at the Temple". The positions of the measured points, presented in figure 1, were selected in close cooperation with the restaurateur. The measurements cover the main colours and in some case some of the different hues.

The results of the measurements are summarized in table I, where the pigments identified at each icon are compared with those identified on the wall paintings of Onufri (Pavlidou et al., 2006 &Civici et al., 2008).

Tabela 1. Pigments identified on each icon

Color	Wall paintings [8,9]	Christ Pantokrator	Presentation at the temple
Red	Red ochre	Red ochre	Red ochre
	Cinnabar	Cinnabar	Cinnabar
	-	Red lead	Red lead
Yellow	-	Gold	Gold
	Yellow ochre	Yellow ochre	Yellow ochre
Green	Green earth	Cu based	Cu based
Blue	Azurite	-	-
White	Ca white	(Pb white)	Pb white
Ground	Calcium carbonate + Gypsum	Gypsum	Gypsum + Pb white

A small number of similar pigments were used for the preparation of both icons. Lead white (basic lead carbonate ($2PbCO_3 \cdot Pb(OH)_2$) for the white color, red lead (Pb_3O_4), cinnabar (HgS) and red ochre for the red color, cooper based pigments for the green color as well as gold and yellow ochre for the yellow color were clearly identified by our measurements. Mixtures of different pigments were also used for obtaining the desired different hues of the colors. These pigments were widely used for icon painting during Byzantine and post Byzantine period (Sotiropoulou & Sister Daniilia, 2010).

In the icon "Christ Pantokrator" we measured the ground layer on a spot of several millimeters that was without the painted layer (p16). The main detected elements were Ca and S, indicating the presence of gypsum with some impurities of Fe and Sr (figure 2). In the icon "The presentation of Christ in the Temple" we couldn't find such a spot and evaluated its composition from the measurement of p28 on the bordure of the icon where the gold layer had fallen. The spectrum at this point, beside Ca and S, showed the presence of relative high amounts of Fe, Au and Pb (figure 2). Au should be related with remains of the gold layer, Fe should come from the red layer (bole) over which the gold layer was applied, while Pb could probably be related with the presence of a thin layer of white lead applied over the gypsum. This practice should have been used on the entire icon as Pb is present in the spectra measured on the golden layer on top of the icon (p3-5), while it is not present on the spectra of the gold layer of the icon "Christ Pantokrator" (figure 4). A similar practice of preparing the ground by applying white lead on gypsum is found in the decorations of the ceiling of Helvetia Tekke in Berat (Merkaj & Civici, 2019) and is also reported by Kouloumpi (Kouloumpi, 2016).

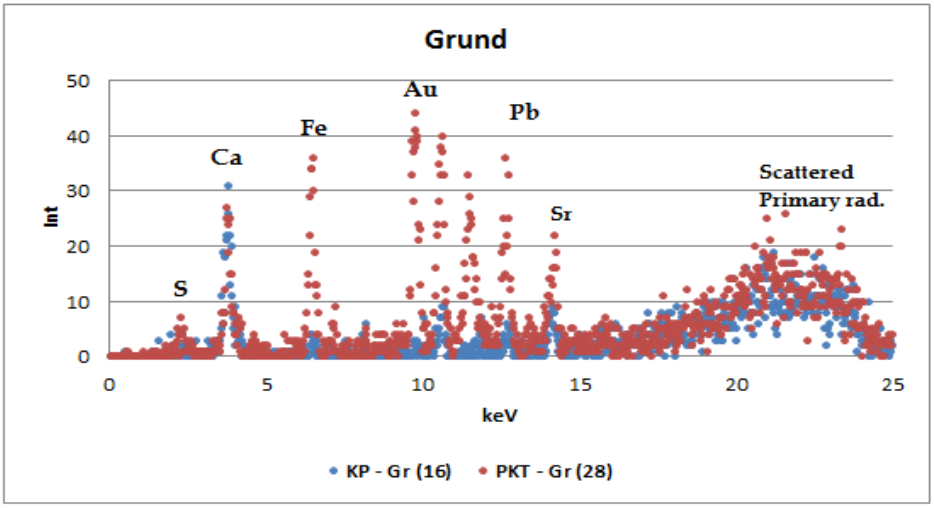

Figure 2. Comparison of the spectra of the ground layer of the icons

White lead is used in both icons for the white colour. The presence of high amounts of Pb in the spectrum measured at the white pages of the Gospel in the icon "Christ Pantokrator" (p12) indicates the application of white lead (figure 3). In the icon "The presentation of Christ in the Temple" we couldn't measure any white spot but the presences of Pb in most of the spectra from different colours suggest the use of white lead as a base pigment. In figure 3 are presented the relative intensities of the elements in the spectra measured on a few grey coloured areas of this icon (p13, p20, p21, p23), which show the predominance of Pb. This suggests that white lead was mixed with black pigment (most likely carbon black) for the preparation of grey.

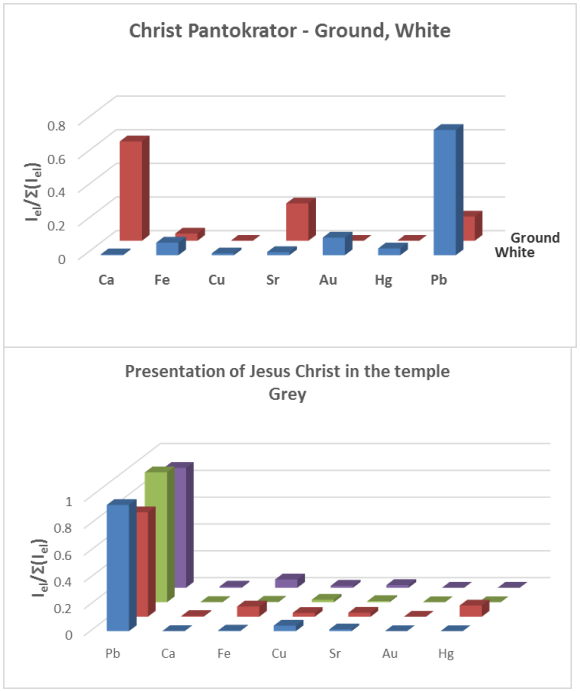

Figure 3. The relative intensities of the elements in the spectra of ground layer, white and grey colours from both icons

In figure 4 are presented the relative intensities of the spectra measured at different yellow gold coloured areas in both icons (KP 2, 5 and PKT 3, 4, 5, 29). Gold is the main element in all the spectra confirming the presence of the gold foil. It is observed that the relative intensities of Au in the spectra measured on the icon "Christ Pantokrator" are much higher than those measured on the other icon. This can be an indication of the thickness of the gold foil.

It appears that the gold layer in the icon "Christ Pantokrator" is rather thick and it sufficiently absorb the radiation emitted by the elements related with the

underneath layers, while the gold layer in the icon "The presentation of Jesus Christ in the Temple" is very thin and rather high intensities of Ca, Sr, Fe and Pb are present in the spectra. As mentioned above, Ca, Sr and Pb are coming from the ground layer while the presence of Fe is related with a red layer known as bole (a kind of red ochre rich in Fe) over which was applied the thin gold foil.

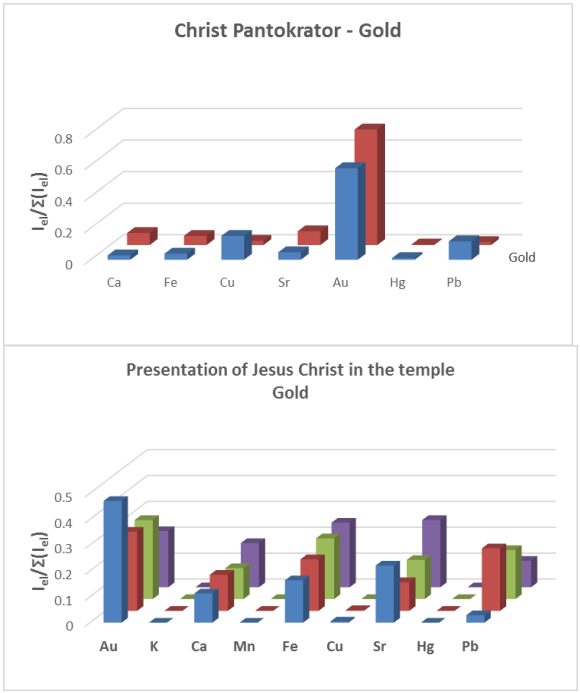

Figure 4. The relative intensities of the elements in the spectra of gold painted areas

In both icons there are some yellow areas that are not prepared with gold (KP-7 and PKT-17, 15). The presence of Fe in the spectra of these yellow areas confirms the use of yellow ochre ($FeO(OH)\cdot nH_2O$). The light yellow hues are prepared by mixing the yellow ochre with white lead and in some cases thin layers of white lead are applied directly over the yellow ochre (PKT p17). This explains the high presence of Pb in those spectra (figure 5). Similar spectra were obtained by the measurements on the areas with flesh tones (incarnato) in the icon "Christ Pantokrator" (KP-9, 14, 15, 21, 22) (figure 5). Those spectra suggest the preparation of the flesh tones by mixing yellow ochre with small amounts of black and red pigments (cinnabar or red ochre).

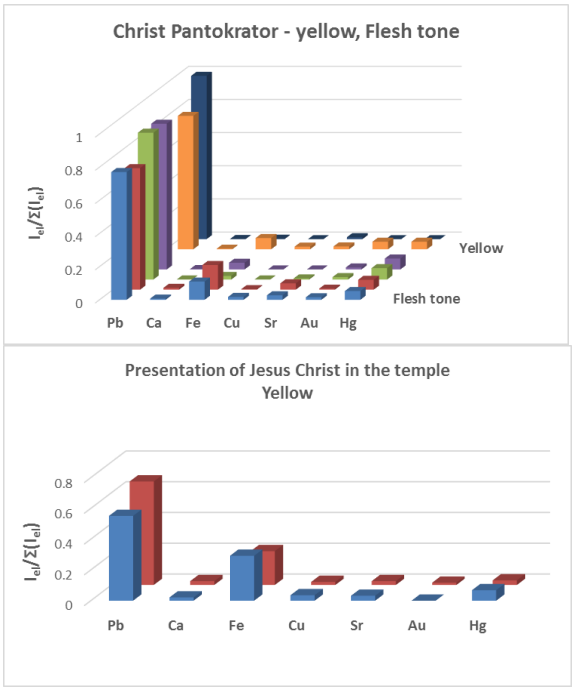

Figure 5. The relative intensities of the elements in the spectra of yellow painted areas

The green colour is widely used in both icons and a cooper based pigment is used in all areas as indicated by the presence of high amounts of Cu in the spectra of green coloured areas (figure 6). There are two different Cu based green pigments used during the middle ages, malachite (copper carbonate hydroxide mineral $Cu_2(CO_3)(OH)_2$) and vert-de-gris an artificially produced basic copper acetate ($Cu(CH_3COO)_2.nCu(OH)_2$), which can't be distinguished by XRF. Different hues of green are prepared by the mixture of the Cu based green with white lead. This green pigment mixed with black pigment is used in the icon "The presentation of Jesus Christ in the temple" in all dark areas (supposed to be in the shadow) (PKT-13, 16, 18, 22).

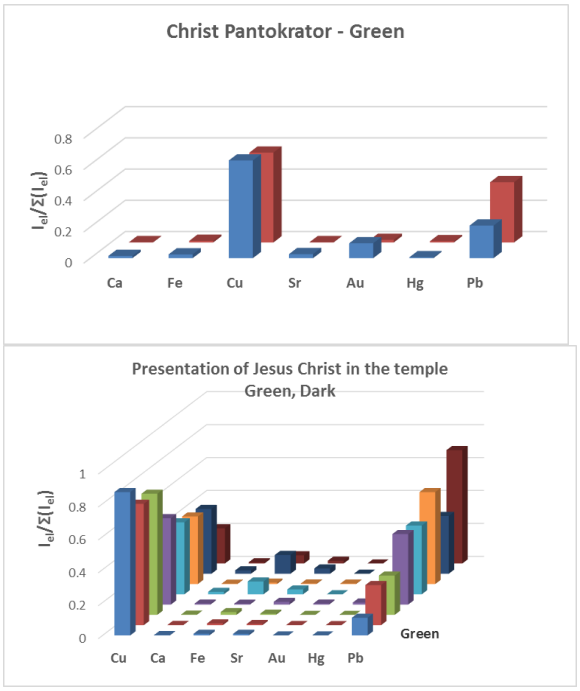

Figure 6. The relative intensities of the elements in the spectra of green painted areas

The red colour is widely used in the icons. Onufri have used in his paintings a wide range of red nuances from dark to bright red depending on the situation and the personage. Especially characteristic in his icons is the bright red, which generally is used over or close to gold painted areas and is considered by some authors as "Onufri's trademark red" (Drishti , 2017). This bright, warm red colour is clearly seen in both icons (PKT-1, 2, 12, 14 and KP-1, 10).

The relative intensities of the spectra measured on those areas, presented in figure 7, show Hg as the main element, indicating the use of the red pigment cinnabar (HgS) mixed with small amounts of white lead. Pb appears to be the main element of the spectra measured on the Christ's dress in the icon "Christ Pantokrator" (KP-6, 8, 23) and in other points with similar nuance in the icon "The presentation of Jesus Christ in the Temple" (PKT-8, 9, 10, 11, 26). This indicates the use of the pigment red lead (Pb_3O_4) in those areas, sometimes mixed with white lead and small amounts of other pigments (Fe, Cu, Hg). The measurements indicate that red ochre (Fe_2O_3) was used for the dark red colour of the Virgin's himation and the reddish floor in the icon "The presentation of Jesus Christ in the Temple". Fe appears to be the main element in those spectra (figure 7).

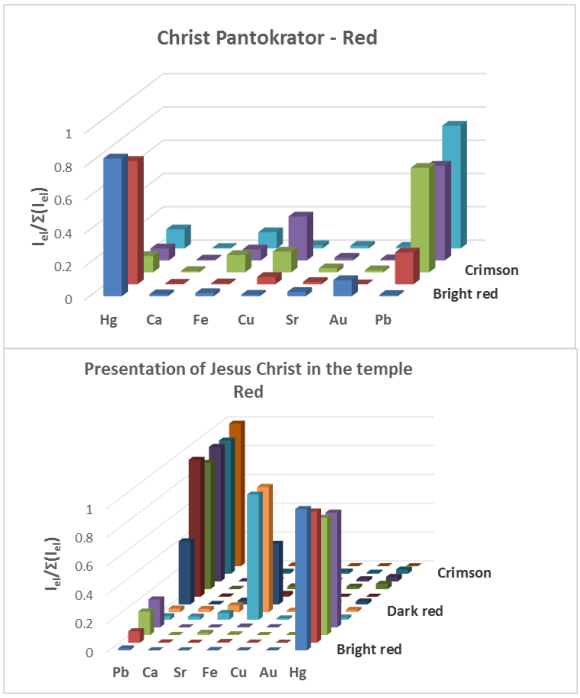

Figure 7. The relative intensities of the elements in the spectra of red painted areas

The composition of the silver foil that covers the upper part of the icon "Christ Pantokrator" was determined based on the in-situ measurements performed at three different points on the foil's surface without any preparation. The calculation of the concentrations was made in our lab following a quantitative procedure used for the determination of the composition of the silver coins (Civici et al., 2007). The results indicate the metal foil is made of silver (85 – 90%), cooper around 2% and gold (10 – 12%). These results should be considered as indicative because of several reasons. First, the measured surface was quite oxidized which can probably lead to changes of the composition on the surface and another important reason is that with much probability the silver foil was gilded and gold comes from the upper layer which is deteriorated.

Conclusions

XRF is successfully used for the identification of the painting materials in two icons attributed to the famous 16th century Onufri. In both icons the paintings were prepared using the tempera technique. Differences in the preparation of the ground layers were observed between the icons. In both of them the basic part of the ground layer was prepared with Gypsum, identified by the presence of Ca

and S, but in the icon "The presentation of Christ in the Temple" gypsum is covered with a thin layer of lead white.

A small number of similar pigments were used for the preparation of both icons. Lead white for the white color, red lead, cinnabar and red ochre for the red color, cooper based pigments for the green color as well as gold and yellow ochre for the yellow color were clearly identified by our measurements. Mixtures of different pigments were also used for obtaining the desired different hues of the colors. These pigments were widely used for icon painting during Byzantine and post Byzantine period.

The identified pigments from the icons are similar with those identified in the wall paintings of Onufri (Civici & Anastasiou & Zorba & Paraskevopoulos & Dilo & Stamati & Arapi, 2008; Franceschi & Nole & Vassallo, 2012), presented in table I. The differences that are observed in three types of pigments (white, green and red) can be explained with the different painting techniques (earthen pigments are more compatible with the fresco) and/or economic reasons.

Acknowledgements

The authors would like to thank Mr. G. Treska, restorer/conservator from the Institute of Cultural Monuments in Tirana, as well as the local staff of the Onufri museum in Berat for their support and assistance during the examinations. The spectrometers of the XRF laboratory of the Institute of Applied Nuclear Physics of Tirana University were used in this work.

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